Normalization of the Fox–Goodwin Algorithm to Calculate Scattering Matrices in an Adiabatic Basis at Low and High Collision Energies

J. P. BRAGA* and J. C. BELCHIOR

Departamento de Química–ICEx, Universidade Federal de Minas Gerais, Pampulha (31.270-901), Belo Horizonte, MG, Brazil

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ABSTRACT

Scattering matrices in an adiabatic basis were calculated for a model two-state atomic collision using a simple modification (normalization of the wave function) of the Fox–Goodwin three-point recurrence relation. Unlike the previous application of this method to scattering the present algorithm was able to precisely calculate the scattering matrix not only at low collision energies (eV), but also at high energies (keV). An analysis of the convergence of the modified Fox–Goodwin algorithm is also discussed for several angular momenta and for several energies where the results were compared to the renormalized Numerov method. © 1996 by John Wiley & Sons, Inc.

Introduction

The sixth-order normalized Numerov method, proposed by Johnson,[1] is a very useful method to calculate scattering matrices since it combines stability in the closed channels region and simplicity for programming. This method has been used to calculate scattering matrices and position of bound states.[2] It aims to solve the Schrödinger equation in a diabatic basis, but this representation may be not always be convenient, which is the case, for example, in the charge transfer process of He–He-like collision dynamics where the rotational and radial coupling are available.[3]

For inelastic and reactive scattering it is recognized that the R matrix approach, proposed by Light and Walker,[4] and the generalized log derivative method of Mrugala and Secrest,[5,6] are very stable and efficient methods. However, the simplicity of the normalized Numerov method also provides a simple and stable way to propagate the wave function, which makes this latter method more attractive.

This study will investigate a reliable procedure for calculating the scattering matrix in an adiabatic

* Author to whom all correspondence should be addressed.

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basis by modifying the Fox–Goodwin[7] algorithm which is based in a three-point recurrence relation. This algorithm has been used in the past to calculate bound states[8] but it was applied to evaluate the scattering matrix for low collision energies.[9] In Ref. 9 it was argued that the Fox–Goodwin algorithm is not a good method to calculate scattering matrices at high collision energies. In fact, even at low collision energies, the aforementioned investigators found instability in the Fox–Goodwin algorithm due to the classical forbidden region. It will be shown that a simple modification of this method can give a very reliable algorithm which does not possess the problems discussed in Ref. 9. The algorithm will be tested for a two-state model where the diabatic representation is possible. Exact results will then be taken as the numerical solution of the sixth-order renormalized Numerov method.

Adiabatic Representation for a Model System

To establish the procedure for describing the adiabatic representation we first write the Schrödinger equation in the diabatic basis:

$$\frac{d^2}{dR^2}\mathbf{u}(R) + \mathbf{Q}_D(R)\mathbf{u}(R) = 0 \tag{1}$$

where $\mathbf{Q}_D(R)$ is given by:

$$\mathbf{Q}_D(R) = k^2\mathbf{I} - \frac{l(l+1)}{R^2}\mathbf{I} - \frac{2\mu}{\hbar^2}\mathbf{V}(R) \tag{2}$$

and μ is the reduced mass of the system, and $k^2\mathbf{I}$ is a diagonal matrix which contains the collision energy and the energy of the channel. The matrix $\mathbf{V}(R)$ contains the potentials and will be responsible for the transitions between the states. If the diagonalization of this matrix is carried out one can work on this new basis at the expense of having nondiagonal terms in the kinetic nuclear operator.

Using the following transformation:

$$\mathbf{U}(R)^{-1}\mathbf{V}(R)\mathbf{U}(R) = \mathbf{D}(R) \tag{3}$$

it is straightforward to obtain the Schrödinger equation in the adiabatic representation given by:

$$\frac{d^2}{dR^2}\mathbf{X}(R) + 2\mathbf{A}(R)\frac{d}{dR}\mathbf{X}(R) + \mathbf{Q}_A(R)\mathbf{X}(R) = 0 \tag{4}$$

where $\mathbf{X}(R) = \mathbf{U}(R)^{-1}\mathbf{u}(R)$, and:

$$\mathbf{A}(R) = \mathbf{U}(R)^{-1}\frac{d}{dR}\mathbf{U}(R) \tag{5}$$

The $\mathbf{Q}_A$ matrix is now defined as:

$$\mathbf{Q}_A(R) = \mathbf{A}^2(R) + \frac{d\mathbf{A}(R)}{dR} + k^2\mathbf{I} - \frac{l(l+1)}{R^2}\mathbf{I} - \frac{2\mu}{\hbar^2}\mathbf{D}(R) \tag{6}$$

The above quantities will be calculated for the classical HeNe[10,11] collision problem which has been used several times as a test model. A simple model, like He–Ne collision, is just used because, for this particular problem, the diagonalization can be performed. However, this diagonalization is not always possible. For example, we have recently carried out calculation of a charge transfer process where rotational and radial coupling are present.[12] In such a calculation the simultaneous diagonalization of these couplings cannot be performed and therefore one is forced to work on the adiabatic basis to do scattering calculations. For this case the Numerov method is useless.

The interaction potential in the diabatic basis, for the present study, is written as[10]:

$$\begin{aligned} V_{11} &= 21.1R^{-1}\exp(-R/0.678) \\ V_{22} &= (21.1R^{-1} - 12.1)\exp(-R/0.678) + 0.617 \\ V_{12} &= 0.170\exp(-R/0.667) \end{aligned} \tag{7}$$

where all quantities are in atomic units.

For the two-state model defined in eq. (7), the following coupling matrix is obtained:

$$\mathbf{A}(R) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\frac{d\gamma}{dR} \tag{8}$$

where the parametric angle is written as:

$$\gamma = \frac{1}{2}\tan^{-1}\left(\frac{2V_{12}}{V_{22} - V_{11}}\right) \tag{9}$$

Normalized Fox–Goodwin Algorithm

For deriving the numerical algorithm it is convenient to transform the adiabatic equation into a form given by:

$$\mathbf{E}(R)\mathbf{X}(R+h) + \mathbf{F}(R)\mathbf{X}(R) + \mathbf{G}(R)\mathbf{X}(R-h) + O(h^n) = 0 \tag{10}$$

where h is the stepsize for the integration and $\mathbf{E}(R)$, $\mathbf{F}(R)$, and $\mathbf{G}(R)$ are matrices to be established. In one dimension there is no need to look for this three-point recurrence relation since the first derivative can always be removed by a suitable transformation,[13] although there is an algorithm of the sixth order that establishes the above equation in one dimension.[14] For more than one dimension there is also an algorithm of sixth order,[15] but it requires 19 inversions per step and, consequently, it will be very time consuming. The normalized Fox–Goodwin algorithm will, instead, require only three inversions. Using the Schrödinger equation in an adiabatic basis [eq. (4)], the following equation can be written:

$$\begin{aligned}\frac{1}{2}(\mathbf{X}(R+h)+\mathbf{X}(R-h))-\mathbf{X}(R)&\\ +\frac{h}{4}\mathbf{P}(R)(\mathbf{X}(R+h)-\mathbf{X}(R-h))&\\ +h^2\mathbf{Q}_A(R)\mathbf{X}(R)&\\ =\frac{h^4}{6}\mathbf{P}(R)\mathbf{X}^{(3)}(R)+\frac{h^4}{24}\mathbf{X}^{(4)}(R)&\\ +\frac{h^6}{120}\mathbf{P}(R)\mathbf{X}^{(5)}(R)+\frac{h^6}{720}\mathbf{X}^{(6)}(R)&\\ +O(h^8)&\end{aligned} \tag{11}$$

where:

$$\mathbf{P}(R)=2\mathbf{A}(R)=2\left(\mathbf{U}^{-1}\frac{d}{dR}\mathbf{U}\right) \tag{12}$$

and (n) stands for the nth derivative of the function. Ignoring the terms on right-hand side of eq. (11) and rearranging the results, one obtains:

$$\left(\mathbf{I}+\frac{h}{2}\mathbf{P}(R)\right)\mathbf{X}(R+h)+(h^2\mathbf{Q}_A(R)-2\mathbf{I})\mathbf{X}(R)+\left(\mathbf{I}-\frac{h}{2}\mathbf{P}(R)\right)\mathbf{X}(R-h)=0 \tag{13}$$

The above equation is rearranged to obtain:

$$\begin{aligned}\mathbf{R}(R+h)=&\left[\mathbf{I}+\frac{h}{2}\mathbf{P}(R)\right]^{-1}\left[2\mathbf{I}-h^2\mathbf{Q}_A(R)\right]\\ &-\left[\mathbf{I}+\frac{h}{2}\mathbf{P}(R)\right]^{-1}\\ &\times\left[\mathbf{I}-\frac{h}{2}\mathbf{P}(R)\right]\mathbf{R}(R-h)^{-1}\end{aligned} \tag{14}$$

with:

$$\mathbf{R}(R)=\mathbf{X}(R+h)\mathbf{X}(R)^{-1} \tag{15}$$

The initial condition for the wave function gives the seed for the above recurrence relation:

$$\mathbf{R}(0)^{-1}=0 \tag{16}$$

This initial condition, plus one-point recurrence relation [eq. (14)] are the basic equations for the renormalized Fox–Goodwin algorithm.

At a large scattering coordinate the two representations coincide and the reaction matrix $\mathbf{K}$ is obtained as usual[2]:

$$\begin{aligned}\mathbf{K}=&-[\mathbf{R}(R_{max}-h)\mathbf{N}(R_{max}-h)-\mathbf{N}(R_{max})]^{-1}\\ &\times[\mathbf{R}(R_{max}-h)\mathbf{J}(R_{max}-h)-\mathbf{J}(R_{max})]\end{aligned} \tag{17}$$

where R_{max} is the maximum scattering coordinate and $\mathbf{N}(R)$ and $\mathbf{J}(R)$ are diagonal matrices that contain the Riccati–Bessel functions.[16] These functions were generated by forward and backward recurrence relations.

Results

For analyzing the normalized Fox–Goodwin method in an adiabatic representation we calculated the transition probability at 70.9 eV of collision energy for the potential given in eq. (7). Integration was performed for a maximum value of 15 a.u. for the scattering coordinate with a step size of 0.001 a.u. Table I shows the results for different angular momenta and the transition probabilities for two different step lengths in an adiabatic representation. As can be seen, for obtaining the same accuracy, one needs to use a step size at least 100

TABLE I.
Transition Probabilities at 70.9 eV Calculated in a Diabatic Basis Using Numerov of Sixth Order ($|S_{12}|^2_a$) and on an Adiabatic Basis Using the Normalized Fox–Goodwin Algorithm for $h = 10^{-3}$ a.u. ($|S_{12}|^2_b$) and $h = 10^{-5}$ a.u. ($|S_{12}|^2_c$).

l	$\lvert S_{12}\rvert^2_a$	$\lvert S_{12}\rvert^2_b$	$\lvert S_{12}\rvert^2_c$
0	2.854 (−4)	2.814 (−4)	2.854 (−4)
10	1.656 (−3)	1.684 (−3)	1.657 (−3)
20	1.108 (−2)	1.106 (−2)	1.108 (−2)
100	7.363 (−2)	7.364 (−2)	7.363 (−2)
200	2.156 (−2)	2.155 (−2)	2.156 (−2)
320	9.408 (−2)	9.408 (−2)	9.408 (−2)

times smaller than that used for the Numerov sixth order and this was necessary to achieve four significant figures in the S matrix.

Certainly the present algorithm does not claim to be faster than the renormalized Numerov method but an alternative approach whereas the latter is not applicable. The relative time consuming, at 70.9 eV and $l = 100$, to obtain the same accuracy is about six times. Henceforth the Fox–Goodwin method is, as expected, slower than the Numerov method.

Figure 1 shows the transition probabilities as a function of angular momentum for a collision energy of 30 eV. It can be seen that the results obtained in an adiabatic representation deviate slightly from the results carried out in a diabatic basis. The step length used in an adiabatic basis was five times greater than that used by the Numerov of order six. The state-to-state cross-section at this collision energy in a diabatic basis is 0.1826 Å^2 and 0.1830 Å^2 in an adiabatic representation. Therefore a relative error of less than 1% is obtained even for larger step size.

In Table II we show the results for high collision energy when comparing the diabatic and adiabatic methods. As can be seen, the normalized Fox–Goodwin algorithm is very accurate and also stable, even for very high collision energies. Such an accuracy on an adiabatic basis and at high collision energy was not obtained by the investigators in Ref. 9, as mentioned before. That was probably due to the fact that, at high collision energies, the wave function oscillates very fast and propagation of the wave function itself is not appropriate. On the other hand, normalization of this wave function provides a very stable method since, in this case, we are propagating numbers close to unity.

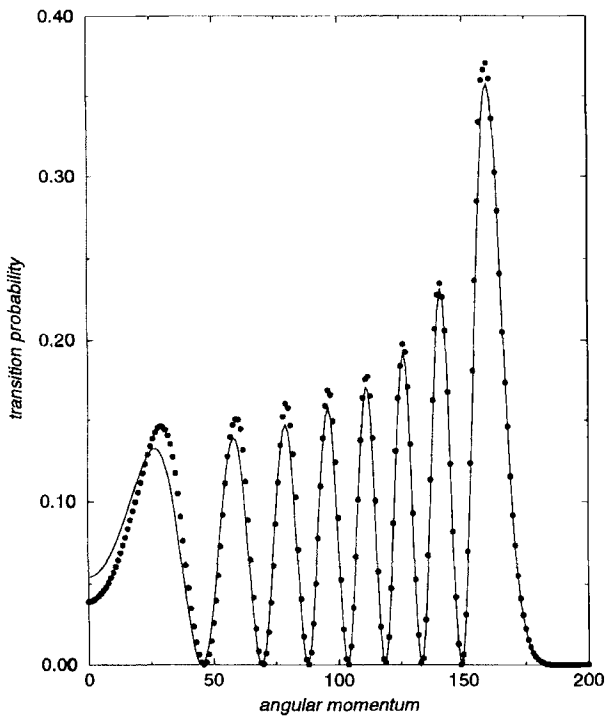

FIGURE 1.

TABLE II.
Transition Probabilities Evaluated on a Diabatic and Adiabatic Representation for Several Angular Momenta and Different Collision Energies.

E / eV	l	Diabatic $\lvert S_{12}\rvert^2$	Adiabatic $\lvert S_{12}\rvert^2$
1000	0	3.522×10^{-3}	3.524×10^{-3}
	100	6.242×10^{-3}	6.245×10^{-3}
	200	1.473×10^{-2}	1.473×10^{-2}
	600	1.136×10^{-2}	1.136×10^{-2}
2000	0	6.129×10^{-3}	6.143×10^{-3}
	100	1.155×10^{-2}	1.155×10^{-2}
	200	1.099×10^{-2}	1.099×10^{-2}
	600	6.360×10^{-8}	5.902×10^{-8}
5000	0	1.531×10^{-3}	1.534×10^{-3}
	100	3.507×10^{-3}	3.504×10^{-3}
	200	3.417×10^{-3}	3.420×10^{-3}
	600	4.335×10^{-3}	4.337×10^{-3}
10,000	0	5.095×10^{-3}	5.094×10^{-3}
	100	4.443×10^{-3}	4.446×10^{-3}
	200	6.111×10^{-4}	6.128×10^{-4}
	600	1.247×10^{-3}	1.249×10^{-3}

Conclusion

In this article, we presented a reliable and simple procedure for integrating the Schrödinger equation in an adiabatic representation which provides accurate transition probabilities compared with the results obtained on a diabatic basis. It is very accurate either at low or high collision energies and also very simple to program. Therefore, due to its simplicity and accuracy, the normalized Fox–Goodwin algorithm might be used as an alternative method to calculate scattering matrices in an adiabatic basis.

Acknowledgments

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